Femtosecond laser texturization for improvement of photovoltaic cells: Black Silicon

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We have irradiated silicon with a series of femtosecond laser pulses to improve light absorption of photovoltaic solar cells. The black silicon shows excellent optical properties on mono and multicrystalline silicon wafers with a reflectivity down to 3 %, without crystal orientation dependence. After the laser process, the front side of samples have been boron-implanted by Plasma Immersion Ion Implantation to create the 3D p+ junction. Improved electrical performances have also been demonstrated with a 57 % increase in the photocurrent, compared to the non-texturized surface.

1. Introduction

The increase of solar cell efficiency is currently investigated by many research groups using different techniques. One possibility is to increase the absorption of light [1-6] by creating a roughening (texturization) of the surface. In recent years, many studies have been performed on the surface texture of silicon wafer [7-10]. In this paper, we enhanced light absorption in the wavelength range corresponding to an AM1.5 solar irradiation spectrum, by creating the texturization with a series of femtosecond laser pulses. Several studies [11-17] have shown that this femtosecond laser treatment, in the presence of a sulfur containing gas (SF_6) is a simple way to texturize the silicon surface. This process produces micro-spikes on the silicon surface (Black Silicon) that strongly reduce the reflection of incident solar light. In the framework of a study related to sustainable development we investigated an alternative to SF_6 gas by working under vacuum with lower cost wafers like multicrystalline (mc-Si) silicon wafers.

2. Experiments

The texturization of the silicon surface was carried out in a vacuum system with a pressure of 5×10^{-5} to 1×10^{-5} mbar.

This low pressure considerably reduces the redeposition of unwanted debris from the laser ablation process [18]. The micromachining experiments were performed using a Ti:sapphire laser (Hurricane model, Spectra-Physics) that was operated at 800 nm, with an energy of 500 μJ, a repetition rate of 1 kHz and a laser pulse duration of 100 fs. To get a more uniform laser energy distribution, only the center part of the gaussian laser beam was selected using a square mask of 2 x 2 mm^2. A spot about 35 x 35 μm^2 area was obtained projecting the mask image onto the sample surface with a lens (f' = 50 mm). Laser beam was perpendicular to the sample surface. A computer-controlled XY-stage (for the sample) and Z-stage (for the objective lens) allowed precise positioning of the spot on surface sample and enabled us to scan the surface at 150 μm/s. The laser energy delivered to the sample surface could be attenuated by coupling an analyzer and a polarizer and completed by a set of neutral density filters (NDF). The analyzer rotation, the opening and closing of shutter placed in front of the polarizer, and the XYZ stages motion were controlled by a computer. The engraving results are in situ monitored by a CCD camera as shown in Fig. 1.
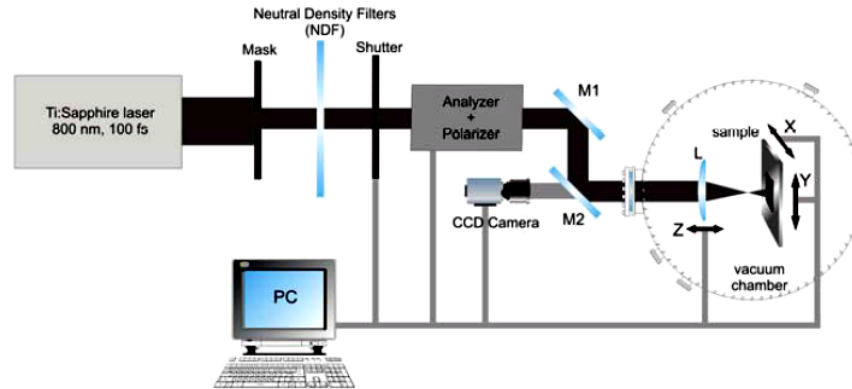
Fig. 1. Experimental set-up.

We have used two types of silicon wafers: <100> monocrystalline silicon (c-Si) and multicrystalline silicon (mc-Si). The wafers have been laser textured on different grains with different crystal orientations, on a 5x5 mm^2 surface: grain 1 is for c-Si and grains 2, 3 and 4 concerns the mc-Si, as shown in Fig. 2. An integrating sphere was used to measure the total R reflectance (specular + diffuse) of the surface, with a spectrophotometer operating between 350 and 1200 nm.
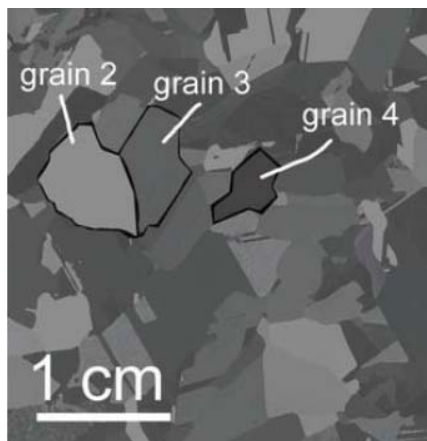
fact that the mc-Si is not polished and has a higher initial absorptivity (R is around 10 % in the visible range for mc-Si and 30 % for the polished c-Si, as shown in Figure 3).
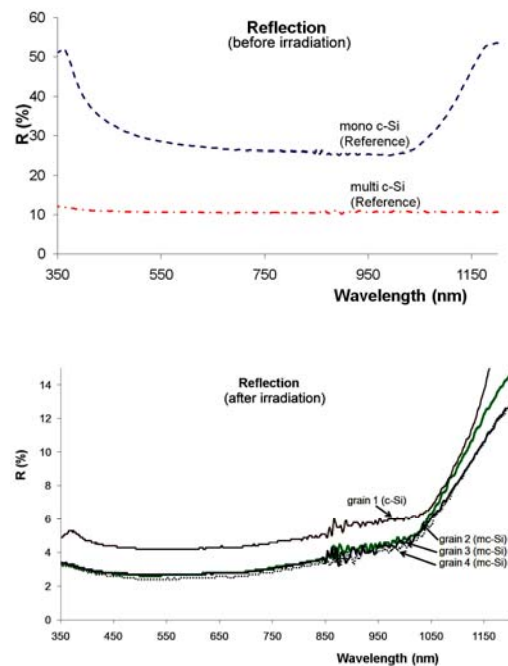

Fig. 3. Reflectance of c-Si and mc-Si, before (left) and after (right) laser texturization measured on c-Si (grain 1) and mc-Si (grains 2,3 and 4); laser conditions: F = 850 mJ/cm^2, 600 shots.

Fig. 2. Photography of a multicrystalline wafer showing the different grains, before laser processing.

3. Results

The different silicon grains were texturized using the same laser irradiation conditions (F = 850 mJ/cm^2, 600 shots, P = 10^{-5} mBar). Figure 3 shows the measured reflectance of the silicon surfaces before (left) and after (right) laser texturization for monocrystalline (c-Si grain 1) and multicrystalline (mc-Si grains 2, 3 and 4) silicon. For both types of samples the reflectance significantly decreases after laser texturization. The improvement is even better with the mc-Si: this can be explained by the

Fig. 4 shows SEM pictures of the c-Si and mc-Si samples before laser texturization. We can see the different initial roughness of the samples. The c-Si is a polished surface and the large roughness of the mc-Si surface is due to the process of cutting ingots into wafer. This initial roughness can explain the difference in laser

energy absorption between the c-Si and mc-Si. If more laser energy is absorbed the created structures are larger (diameter, spacing and height) and consequently absorption increases [18]. This phenomenon can explain the slight difference in the final reflection for the different materials (3 % for mc-Si and 4.5 % for c-Si).
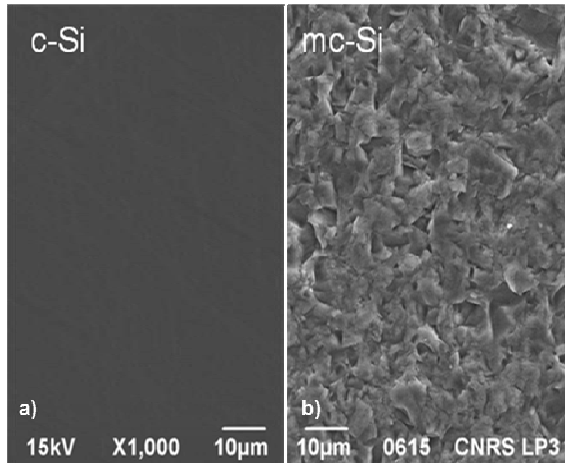

Fig. 4. SEM images of the initial samples: a) C-Si has been polished and b) the mc-Si is already structured due to the slicing of the ingot.
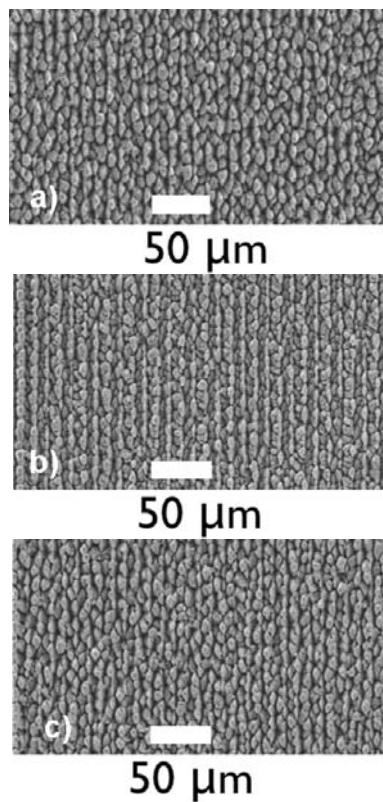

Fig. 5. SEM images of laser texturization on three mc-Si grains a) grain 2, b) grain 3 and c) grain 4, F = 860 mJ/cm², 600 shots.

The laser treatment of the surface of mc-Si has enabled us to decrease the reflection down to 3 % in the visible and UV and 14 % at 1150 nm. For the c-Si (grain 1) the reflection in the UV decreases from 50 % down to 4-5 %. The reflection is equally reduced for all the mc-Si grains (grains 2, 3 and 4 as shown in Figure 3) which mean that the laser texturization is isotropic, as opposed to chemical alkaline etching which depends on the crystal orientation as seen in Figure 7. Moreover, the visual aspect of the treated surfaces (c-Si and mc-Si) is velvet black, without visible specular reflection in any direction.

After laser texturization, the boron doped p+ regions were obtained using a Plasma Ion Immersion technique [18] and metalized to produce a finished photovoltaic cell. The beneficial effect of texturization is demonstrated by the LBIC [18-21] analysis (Light Beam Induced Current). The LBIC allow to measure the photocurrent that is generated after texturization. This photocurrent has been compared to the current generated by non treated areas. The photocurrent gain (%) is plotted in Figure 6, for different laser conditions (600, 1200, 3000 and 6000 shots at a fluence of 200, 500 and 900 mJ/cm²).
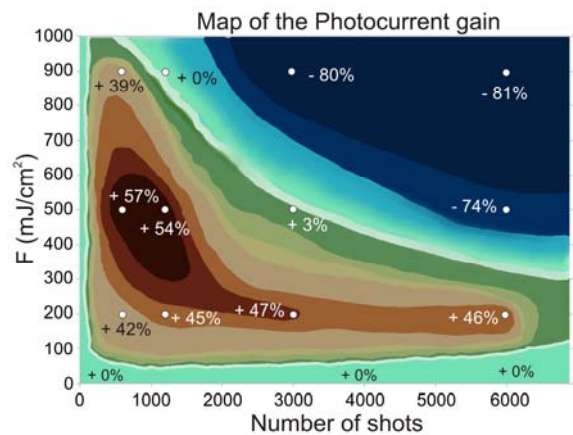

Fig. 6. Improvement (%) of the photocurrent measured by LBIC as a function of the laser parameters: fluence (200, 500 and 900 mJ/cm²) and number of shots (600, 1200, 3000 and 6000), the false colors are simply used as an eye-guide, sample: c-Si.

This diagram shows that for an average fluence of 500 mJ/cm² there is an optimum number of pulses (between 600-1200) for which the photocurrent gain is very high (>50 %). If we increase the number of shots or the fluence we can have a degradation of the photocurrent due to a severe damage of the surface. It is also important to notice that the next step after the texturization is usually the passivation of the silicon (usually coupled with the antireflection coating ARC). In our case textured our surfaces have not been passivated: an additional passivation step would probably improve these results. The use of an ARC is however questionable because the reflectivity of the surface is already very low.

Table 1 summarizes the reflections achieved by different texturing techniques and their characteristics.

One advantage of the laser texturization is that the technique is anisotropic, contrary to chemical (KOH) method (see Fig. 7) which is a selective etching that depends on the crystal orientation. Standard chemical texturizations use a large amount of acids, bases and DI water for rinsing while the laser process is a dry process. Moreover, the laser method could reduce the number of fabrication steps: Indeed, the cutting of the wafer silicon induced surface defects. It must be cleaned and etched before being chemically textured. The laser treatment can be applied right after the sawing. Also thanks to the good optical properties, no anti reflection coating is needed after the laser texturization.
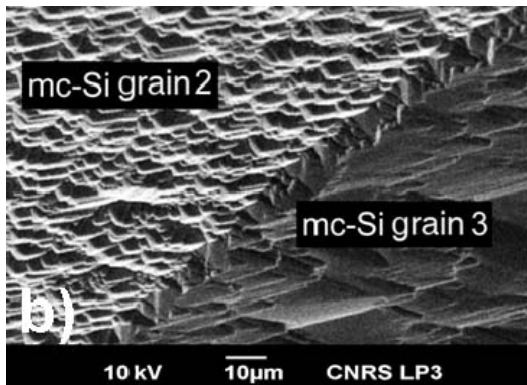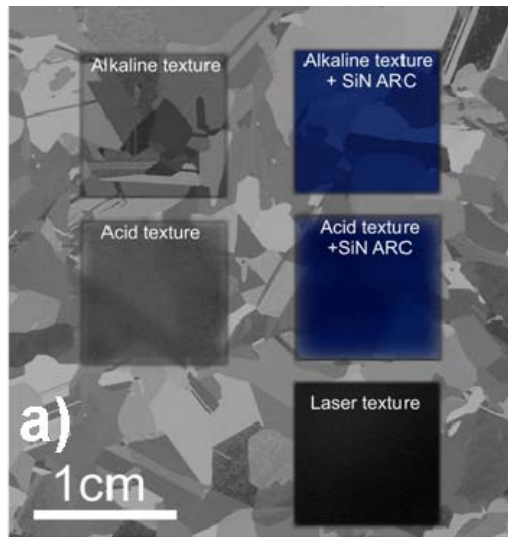

Fig. 7. a) visual aspect of different chemical texturizations (alkaline and acid), with and without ARC and comparison with a laser texture surface, b) SEM view of the grain boundary showing the anisotropy of an alkaline etching.

Table 1. Minimum reflection R % obtained with different texturization techniques.

Texture type	R(%) (in visible)	materials
Laser + SF$_6$ [13]	~1 %	n-type (111) c-Si
Chemical (acid) [6]	10-12	p-type mc-Si
Laser + chemical (base) [7]	8.3 %	p-type mc-Si
Laser (under vacuum)	3 %	p-type mc-Si and (100) c-Si

4. Conclusions

We have prepared laser-microtexturized Si structures which reduce the reflection of silicon surface (black silicon) without using corrosive gases, chemicals and DI water (under vacuum: dry technique). We have worked on both c-Si and mc-Si wafers. Laser texturization does not depend on the crystal orientation which is an advantage for mc-Si solar cells.

The experimental results show that the final reflection of the Si surface is reduced down to 3 % without using anti reflection coating (ARC). The laser parameters (fluence and number of shots) have been optimized to produce a photocurrent gain higher than 50 %.

Experiments are still in progress to make large surface treatment with a fast throughput, in order to quantify the possible benefit on solar cell efficiency.

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