Study On Laser-Induced Periodic Structures And Photovoltaic Application

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Abstract. We have irradiated silicon with a series of femtosecond laser pulses to improve light absorption at the silicon surface. The laser treated surface namely black silicon shows excellent optical properties on mono and multicrystalline silicon wafers with a reflectivity reduction down to 3%, without crystal orientation dependence. After the laser process, the front side of samples has 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 non-texturized surface.

Keywords: Black silicon, femtosecond laser, texturization, solar cell
PACS: 88.40.jj, 81.16.Rf, 78.40.-q

INTRODUCTION

Reduction of optical losses in crystalline and multi-crystalline silicon solar cells by texturing their surface is one of important issues of modern silicon photovoltaics. Several studies [1-7] 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. We used this technique to decrease the reflectance of silicon surface. We fabricate micrometer silicon spikes without corrosive gas by irradiating a silicon surface of crystalline (100) type and mc-Si type, placed under vacuum (10^{-5} mbar), with 800 nm, 100 fs laser pulses. The laser has induced small periodic structures on surface. The smaller structures are called "ripples" and are similar to the capillary waves with a sub-micrometer periodicity (close to the laser wavelength). Ripples found at the bottom of ablated areas are usually attributed to interference between the incident beam and a surface scattered wave [1, 3, 8-12] and have been reported back in the 1960's [13]. In recent investigations [14] on femtosecond ablation from dielectric crystals, Reif *et al* showed that this interpretation may not hold in the case of femtosecond laser pulses. Instead, they suggested self-organization from a surface instability as the origin of the periodic structures. It has been shown that the first ripples are polarization dependent and it is admitted that the formation of these structures occurs a long time after the irradiation of the fs laser pulse. Therefore the

CP1278, *International Symposium on High Power Laser Ablation 2010,* edited by C. R. Phipps

authors suggest that there should be some kind of "polarization memory". They suggest that there may be a diffusion inhomogeneity because of strain fields, either due to the extended defects or induced by the electric field and then persisting, thus serving as the “polarization memorizer”. We studied the formation of the first ripples and the following transformation of these ripples into spikes as a function of laser parameters, such as energy density, numbers of shots, and laser polarization. The surface treated by the laser turns to black when choosing the appropriate parameters. The black silicon shows very good optical properties on mono and multi-crystalline silicon wafers. The laser treatment of the surface of mc-Si has enabled us to decrease the reflection down to 3% [15, 16, 17]. We have also characterized the photocurrent increase by LBIC (Light Beam Induced Current) [18 - 21]. The results have shown an improvement of the photocurrent up to 57 %.

EXPERIMENTS

The texturization of the silicon surface was carried out in a vacuum system with a pressure of $5x10^{-5}$ to $1x10^{-5}$ mbar. This low pressure considerably reduces the redeposition of unwanted debris from the laser ablation process [20]. The micro-machining 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 by projecting the mask image onto the sample silicon 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 sample surface 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).

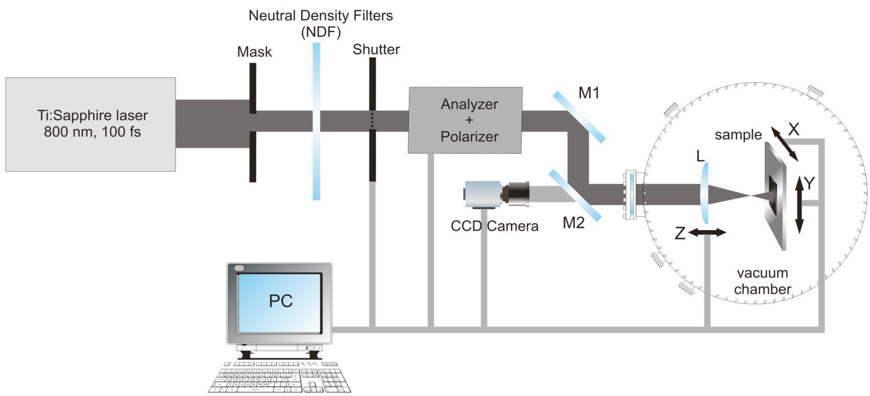

FIGURE 1. Experimental set-up.

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 laser processing are in situ monitored by a CCD camera. The experimental set-up is shown in FIGURE 1

RESULTS

FIGURE 2 shows the ablated areas with laser fluence at F = 300 mJ/cm^2 and for the number of shots ranging from 4 to 600. For smaller number of shots (1 to 3) the ripples are too weak to be seen easily under an SEM. The laser polarization orientation is horizontal. The formation of the fine ripples is clearly visible for 5 shots and more and the orientation of the ripples is perpendicular to the laser polarization. We have measured their periodicity and found an average length of 750 nm (close to the laser wavelength). For higher number of pulses (10 to 50 shots) these ripples tend to collapse to form a more hydrodynamically stable structure, like "beads" [22].

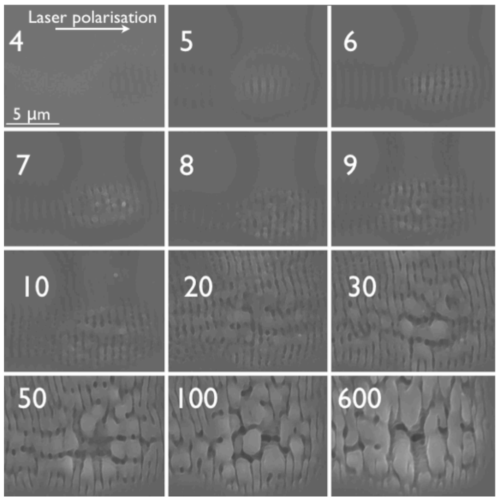

FIGURE 2. Influence of number of shots on the creation of the original fine ripples: fs laser polarization is perpendicular to the structures, laser fluence is identical.

The absorption of the laser light on these beads is not uniform: the ablation is maximized in the valley between the beads which tends to amplify the phenomena and creates more erected structures, i.e. "penguin-like" structures from 600 shots onward.

FIGURE 3 [15] shows the evolution of two cones when the number of shots increases (100, 200, 1000 shots) at F = 900 mJ/cm^2. We can see the collapse between the cones and the result is the formation of a bigger cone.

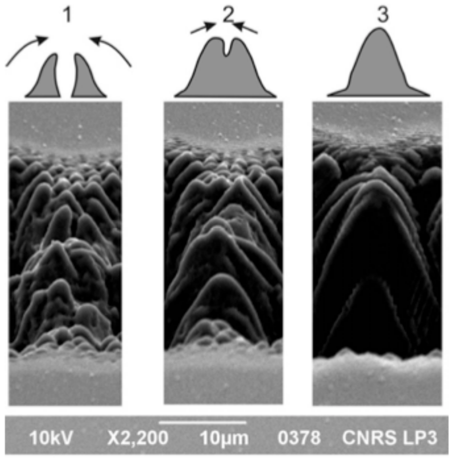

FIGURE 3. Formation of "double cones" 100 fs, 900 mJ/cm^2 (average fluence): 1) 100 shots; 2) 200 shots and 3) 1000 shots.

The evolution of the topography with different fluences is shown on the SEM photos in FIGURE 4 [20]. The size of the structures increases with the fluence. This type of structure tends to enhance the absorption of incident light by multiplied reflections on the structures. We have shown the optical properties (the absorption) change when the size of the spikes increases (height, spacing, diameter). We have measured the absorption gain (between texturized and un-texturized surface) of 56% in the UV and 37% for the visible and IR. The benefit of the texturing on the photocurrent is demonstrated by mapping LBIC (Light Beam Induced Current) as shown in FIGURE 5. This mapping tool has been created to measure the contrast of the photocurrent on multi-crystalline silicon in order to highlight the defects [23]. The LBIC signal indicates the intensity of photocurrent. We can see that it clearly increases in laser treated areas. The photocurrent can increase up to 53 %.

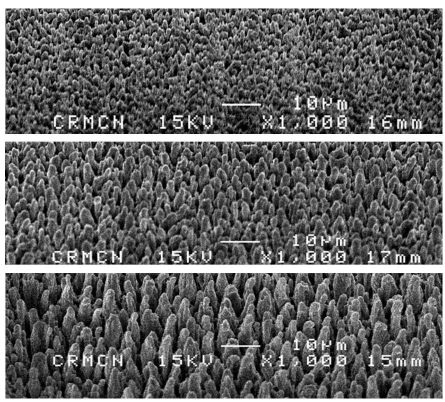

FIGURE 4. SEM photos of texturized surfaces (tilt 50°, same magnification) at different laser fluences: top: 250 mJ/cm^2, middle: 400 mJ/cm^2, bottom: 850 mJ/cm^2.

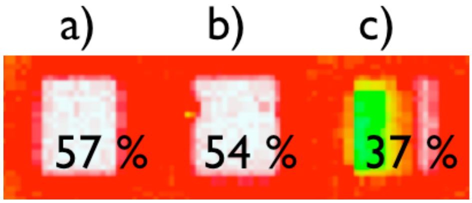

FIGURE 5. LBIC scan maps showing the increase of photocurrent in the laser treated zones, laser fluence F= 185 mJ/cm^2 with: a) 600 shots; b) 1200 shots; c) 3000 shots.

CONCLUSION

We have prepared erected structures structures (Black Silicon) on silicon surface with a femtosecond laser, which significantly reduce the light reflection in the UV, visible and IR band. We have worked both on 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). Also, the laser texturization is a dry technique realized without using any corrosive gases, chemicals or DI water.

The laser parameters (fluence and number of shots) have been optimized to produce a photocurrent gain higher than 57%.

Experiments are still in progress towards realizing large surface treatment with high throughput, in order to quantify the possible benefit on solar cell efficiency.

TEM analysis is also in process to determine the impact of the laser on the material physical properties with a low number of shots. These experiments should give valuable information on the possible in-depth crystallinity changes. The goal is to understand the physical mechanisms accounting for the formation of the ripples.

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