Applied Surface Science 371 (2016) 196–202

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Picosecond laser texturization of mc-silicon for photovoltaics: A comparison between 1064 nm, 532 nm and 355 nm radiation wavelengths

Simona Binetti[a], Alessia Le Donne[a,*], Andrea Rolfi[a], Beat Jäggi[b], Beat Neuenschwander[b], Chiara Busto[c], Cesare Frigeri[d], Davide Scorticati[e], Luca Longoni[e], Sergio Pellegrino[e]

[a] Department of Materials Science and Milano-Bicocca Solar Energy Research Center (MIB-SOLAR), University of Milano-Bicocca, Via Cozzi 55, 20125 Milano, Italy
[b] Bern University of Applied Sciences, Engineering and Information Technology, Institute for Applied Laser, Photonics and Surface Technologies ALPS, Pestalozzistrasse 20, CH-3400 Burgdorf, Switzerland
[c] ENI Spa, Via Giacomo Fauser, 4, 28100 Novara, Italy
[d] CNR-IMEM Institute, Parco Area Delle Scienze 37/A, Fontanini, 43010 Parma, Italy
[e] Laserpoint Srl, Via Della Burrona 51, 20090 Vimodrone, Milano, Italy

ARTICLE INFO

Article history:
Received 27 December 2015
Received in revised form 22 February 2016
Accepted 22 February 2016
Available online 3 March 2016

Keywords:
mc-Silicon
Solar cells
Laser texturing
Picosecond lasers
Subsurface damage

ABSTRACT

Self-organized surface structures were produced by picosecond laser pulses on multi-crystalline silicon for photovoltaic applications. Three different laser wavelengths were employed (i.e. 1064 nm, 532 nm and 355 nm) and the resulting morphologies were observed to effectively reduce the reflectivity of the samples after laser irradiation. Besides, a comparative study of the laser induced subsurface damage generated by the three different wavelengths was performed by confocal micro-Raman, photoluminescence and transmission electron microscopy. The results of both the structural and optical characterization showed that the mc-Si texturing performed with the laser at 355 nm provides surface reflectivity between 11% and 8% over the spectral range from 400 nm to 1 μm, while inducing the lowest subsurface damage, located above the depletion region of the *p*–*n* junction.

1. Introduction

Surface texturing plays a critical role in silicon solar cell performance, as it reduces the optical reflectivity in the whole working range of the device [1,2]. A limitation associated with the use of multicrystalline silicon (mc-Si) solar cells is the inability to effectively texture their front surface with a sufficient decrease of reflectivity [3]. Anisotropic alkaline etching techniques, commonly used to texture monocrystalline silicon, are ineffective on the randomly oriented grains typical of mc-Si wafers [4]. The optimization of a texturing technique able to effectively reduce the optical reflectivity of the Si wafer front surface, regardless of its crystallographic orientation, is therefore a widely investigated topic, being mc-Si the dominant technology for solar cells today [3].

Several techniques were proposed in the literature to texture the mc-Si surface. Among them isotexturing by etching with HNO_3:HF solutions [5], masked isotropic etching [6], mechanical etching [7], reactive ion etching [8] and plasma etching [9]. However, all these techniques involve limitations in size and aspect ratio of texturing.

Laser surface texturing was demonstrated to be applicable, independently of the crystallographic orientation. Two different techniques were exploited by different researchers, i.e. texturing by direct ablation [10,11] and texturing by formation of self organized surface structures [12–15]. A strong reduction of the optical reflectivity in the visible and near infrared spectrum was observed with both techniques used. The first technique is performed both with ns and ultrafast laser sources, and it is usually followed by a chemical etching to remove the superficial damage presented by the formation of a thin defected layer on the top surface, due to the fast quenching of the crystal from the molten phase [11,16,17]. The second technique is preferably performed using ultrafast lasers in the picosecond and sub-picosecond range [12–15]. It is known that different laser parameters, such as fluence, wavelength and polarization, result in a different interaction with the material, i.e. a different heat distribution in the targeted material and, in the case of formation of the self-organized surface structures, it is widely

* Corresponding author. Fax: +39 264485400.
E-mail address: alessia.ledonne@mater.unimib.it (A. Le Donne).

http://dx.doi.org/10.1016/j.apsusc.2016.02.187

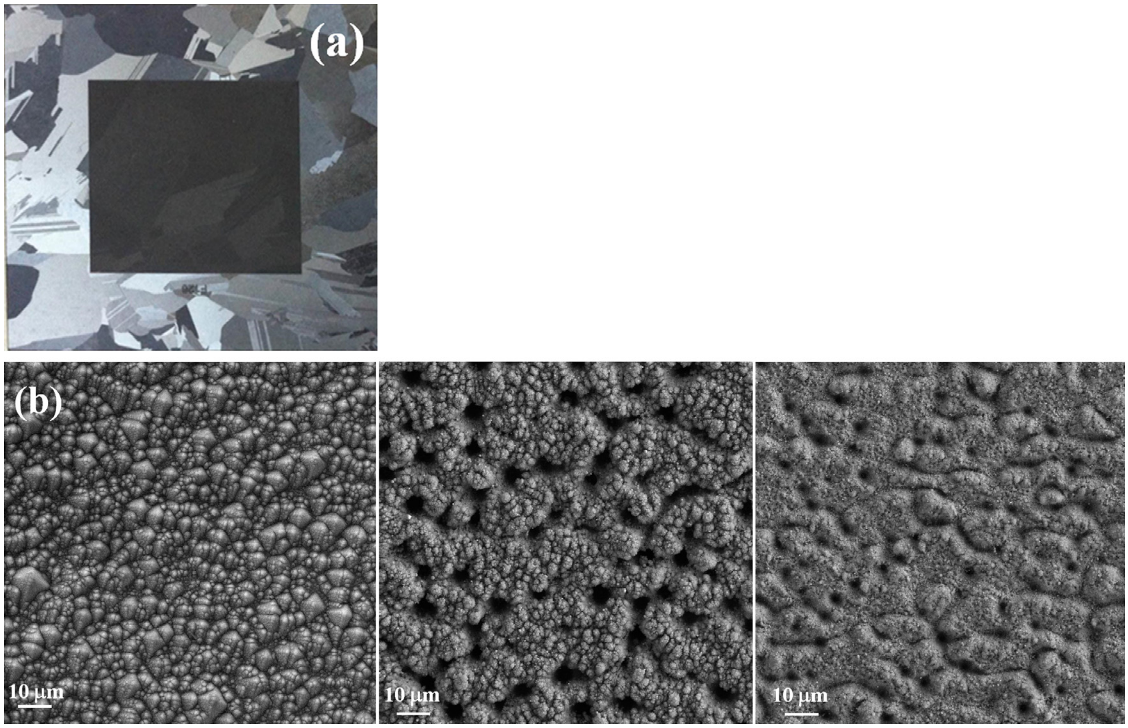

Fig. 1. (a) Picture of a textured mc-Si sample; (b) SEM micrographs of Si areas textured with 355 (on the left; OS = 4, peak fluence: 0.61 J/cm^2), 532 (in the center; OS = 4, peak fluence: 2.18 J/cm^2) and 1064 nm (on the right; OS = 4, peak fluence: 0.97 J/cm^2) laser wavelengths.

accepted that these parameters are associated with the morphology of the obtained superficial structures [18]. Moreover, the effects of different combinations of gases (i.e. SF_6, N_2, etc.) were reported in literature and the effects on the obtained surface structures were studied [19].

However, the occurrence of a laser texturing induced damage was observed, due to the decrease of the open-circuit voltage and fill factor often detected in addition to the desired reflection reduction and current enhancement [20]. Early hypotheses speculated on the formation of dislocations penetrating the junction region [20], while more recent works demonstrated the formation of a mixed amorphous-crystalline silicon layer, whose crystalline volume fraction depends on the pulse duration [21].

Regarding the diffusion of laser induced defects below the surface, the adoption of ultrafast lasers for surface texturing is clearly advantageous over nanosecond laser processing, considering the shorter heating-cooling cycle-time induced during and right after the laser pulses [22,23].

In the present work, surface texturing of mc-Si photovoltaic (PV) absorbers obtained by picosecond laser irradiation using different laser wavelengths was studied and discussed. By adopting a defocused beam, as the processing speed is shown to be primarily limited by the available laser power, the use of a picosecond laser source is more suitable for industrial applications where high throughput is needed, when compared to femtosecond laser sources. Moreover, the lower fluence required to form the self-organized surface structures without creating ablated tracks on the sample enables faster processing time. The fundamental research on the laser-matter interaction specific to picosecond laser irradiation of mc-Si is required to understand the formation and evolution of subsurface laser induced defects which play a direct role in the performance of a functional solar cell. Moreover, the choice of avoiding hazardous gases offers the advantage of a greener and safer process.

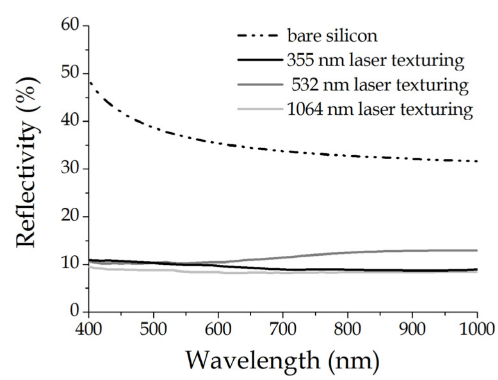

Fig. 2. Spectral reflectivity of mc-Si samples textured with 355, 532 and 1064 nm laser wavelengths (without anti-reflection coating, OS = 4). The reflectivity of bare silicon [14] is also shown for comparison.

2. Material and methods

A commercial Nd:YAG laser amplifier (Fuego® by Time-Bandwidth Products AG) was used to generate linearly polarized laser pulses of about 10 ps with a nearly Gaussian power density profile ($M^2 < 1.3$). The main wavelength of 1064 nm (IR) was converted to 532 nm (Green) and 355 nm (UV) using a second and third harmonic generation box, respectively, while the linearly polarized light was converted to circularly polarized light by adopting a quarter-wave plate.

Galvo-scanners, equipped with telecentric lenses, were employed to scan the laser beam over the surface of the samples. The focal lengths of the telecentric lenses were 100 mm, 160 mm and 100 mm for IR, Green and UV lasers, respectively. The peak fluences of the Gaussian-like beam profile in front of the samples were determined knowing the energy per single pulse and the spot diameter on the target for each different wavelength. All laser