



On the emitter formation in nanotextured silicon solar cells to achieve improved electrical performances



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ABSTRACT

In this paper, we study the effect of an enlarged surface area of nanotextured crystalline silicon wafers on the formation of n-type emitters using a tube diffusion process applying POCl_3 as P dopant source. A fast, single-step and industrially viable F_2 -based dry texturing process is used to perform nanotexturing of Si wafers. This process is presented as an alternative route of nanotexturing in comparison to the two-step nanotexturing approach of creating black silicon and then modifying it with an alkaline or acidic solution. Predictive simulations of phosphorous in-diffusion aided by microscopical characterization of the selected emitters are used to understand the formation of emitter in nanotextured surfaces. Based on these investigations, we show that the optimized emitter leads to a significant improvement in short circuit current density ($J_{sc} \geq 0.7 \text{ mA/cm}^2$) of nanotextured mc-Si solar cells in comparison to the industrial standard acidic textured solar cells.

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1. Introduction

Nanotexturing of crystalline silicon (c-Si) surfaces has been extensively investigated in the past and recent years by applying texturing techniques like reactive ion etching [1,2], plasma-chemical etching [3–5], metal-assisted electrochemical etching [6,7] and laser-assisted texturing [8]. Significant progresses made in optimization of the cell process for nanotextured cells have led towards high conversion efficiencies [6,9]. Very low surface reflection values can be reached for mono c-Si wafers by the formation of black silicon (B-Si) texture, which opens tremendous potential of an improvement in short-circuit current density (J_{sc}) of the solar cells. Multicrystalline silicon (mc-Si) solar cells are supposed to benefit strongly by the application of nanotexturing process because a relatively higher optical loss of an acidic textured surface is one of the main reasons for its overall much lower efficiency in comparison to typical mono c-Si solar cells. Nanotexturing approach for mc-Si surfaces is therefore supposed to enhance the overall cell performance by significantly minimizing the optical losses.

We recently proposed a F_2 -based atmospheric pressure dry etching (ADE) process that combines the cost-effectiveness of a plasma-less atmospheric pressure dry texturing process with an industrial high-throughput inline approach promising high dynamic etch rates [10–12]. The texturing process can be effectively controlled to obtain nanostructures of different surface morphologies and low surface reflection properties. Very recently, we combined this F_2 -based nanotexturing and a short post-etching process to reach 18.0% conversion efficiency (η) for mc-Si solar cells with aluminum back-surface field (Al-BSF), with an absolute gain of up to 0.3% compared to the acidic textured solar cells [13]. Other recent works have also shown significant improvement in η by forming black silicon nanotexture using metal assisted etching process [7,14] or plasma based etching methods [15,16], which is then followed by a post-etching procedure using either alkaline or acidic solutions. Although this texturing approach has already shown a promise of significantly enhancing the η of the mc-Si solar cells, a simple-one step nanotexturing process is even more attractive in both technological and economical points of view. Although such a single-step nanotexturing for mc-Si has been investigated by several groups in the past [2,3,17,18], the texturing methods used in those works are difficult to apply in an industrial scale, mainly due to economic

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prospects (high cost of ownership) and/or environmental concerns (use of high global warming potential gases like SF₆, CF₄, NF₃).

In this paper, we present single-step plasma-less dry texturing method as an alternative method of nanotexturing the c-Si surface to achieve higher J_{sc} values. This single step texturing approach requires removal of a very low amount of Si in order to reach low surface reflection values. Such a fast etching step allows high throughput for large-scale industrial applications. Here, we discuss about the challenges imposed by this single step nanotexturing process to the subsequent solar cell process steps – especially surface passivation and emitter formation processes. The emitter formation in nanostructured surface is discussed in detail. We start the optimization of the emitter by predictive simulations of the phosphorous in-diffusion and emitter formation. The optimized emitter diffusion process is used to fabricate nanotextured mc-Si Al-BSF solar cells and the electrical characteristics are compared to that of reference acidic textured solar cells. Electron beam induced current (EBIC) method is then used to perform a microscopic characterization of the emitter and the simulated and experimental observations are used to provide insights to reach full potential of F₂-based nanotextured surface for mc-Si solar cells.

2. Surface passivation of single-step nanotextured surfaces

We use $\langle 100 \rangle$, p-type, 1 Ω cm float-zone (FZ) c-Si wafers of 250 μ m initial thickness in order to investigate the influence of the single-step nanotexturing process on the morphology and electrical behavior of the c-Si solar cells. All the wafers are saw-damage etched before the dry texturing process. The test wafers are dynamically etched on both sides at the set wafer temperature of 200 $^{\circ}$ C using an effective F₂-concentration of 5% applying the plasma-less atmospheric pressure dry etching (ADE) technique. Since the etching process is single sided, we first etch one wafer side and subsequently the other wafer side. Nanostructures with different surface enlargement ratios are formed on c-Si surface by varying the etching duration. The surface morphology is investigated by Scanning Electron Microscopy (SEM) (Hitachi SU-70) and the surface reflection is measured using spectrophotometer in an integrating sphere (Varian Cary 5000). The weighted surface reflection (R_w) values in the wavelength spectrum of 300–1200 nm are estimated from reflection measurements performed after the texturing process by using the IQE of a standard mc-Si solar cell under AM 1.5G spectrum [19]. The surface enlargement factor of nanostructures is estimated by Atomic Force Microscopy (Dimension 3100, Digital Instruments) using super sharp tip (Nanosensors SSS-NCH) with tip radius < 2 nm and operating in the tapping mode. Since the tip of atomic force microscope might not reach the extreme points of the deep nanostructures, the measurement should be interpreted only as the minimum value of surface enlargement factor. Fig. 1 shows the R_w values of the nanostructures formed by removing different amounts of Si during the texturing process. With an increasing amount of Si removal during the texturing process, R_w falls exponentially from $\approx 18\%$ down to $\approx 2\%$. For comparison, R_w values of the alkaline and acidic textured wafers are measured to be ≈ 10 –11% and ≈ 24 –27% respectively. The exponential reduction in the reflection values can be initially explained by an increase in the depth of nanostructures with an increasing duration of etching. Even longer etching duration further lowers the surface reflection of the c-Si surface and is likely to be driven by the gradual increase in density of nanostructures per unit area.

In Fig. 1, it is obvious that although the deeper nanostructures promise nearly perfect optical confinement, they leave a greatly enlarged c-Si surface behind. Deep nanostructures with very low R_w show high values of minimum surface enlargement factor of up to ≈ 2.3 in comparison to ≈ 1.3 measured for the alkaline texture

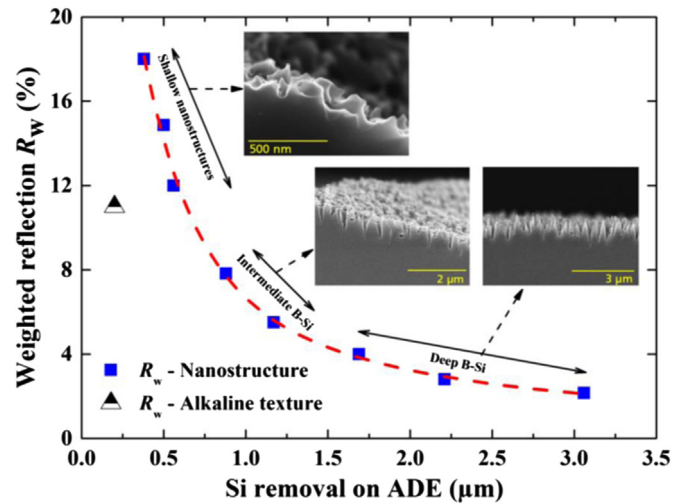


Fig. 1. Weighted surface reflection (R_w) of nanostructures formed by different amount of Si removal during the nanotexturing process. The plot in this range of the parameter variation can be very well fitted by using an exponential decay function. For comparison, R_w of alkaline textured wafer is also plotted. No coating is present on the textured surfaces.

on mono c-Si. Only the shallow nanostructures that are formed with less than ≈ 0.7 μ m of average Si removal show comparable or lower minimum surface enlargement factors than the alkaline textured wafer. An increasing surface area increases the amount of surface defects/dangling bonds at the Si surface, which act like active recombination centres for the photo-generated charge carriers near the Si surface.

In order to understand the influence of surface texturing on the lifetime of minority charge carriers, symmetrical test structures are prepared on p-type, 1 Ω cm FZ c-Si wafers. The wafers are textured on both sides by using ADE process, changing the process duration to form nanostructures of different aspect ratios. After cleaning the wafers in HNO₃/HF based solution, both surfaces are then passivated by 10 nm plasma-assisted atomic layer deposited (p-ALD) AlO_x layers followed by 70 nm PECVD SiN_x layers. A stack of ALD AlO_x/PECVD SiN_x layers is chosen as it is previously observed that PECVD SiN_x alone is unable to form a conformal passivation layer in single-step nanotextured surfaces [11]. In order to emulate the standard Al-BSF solar cell fabrication process,

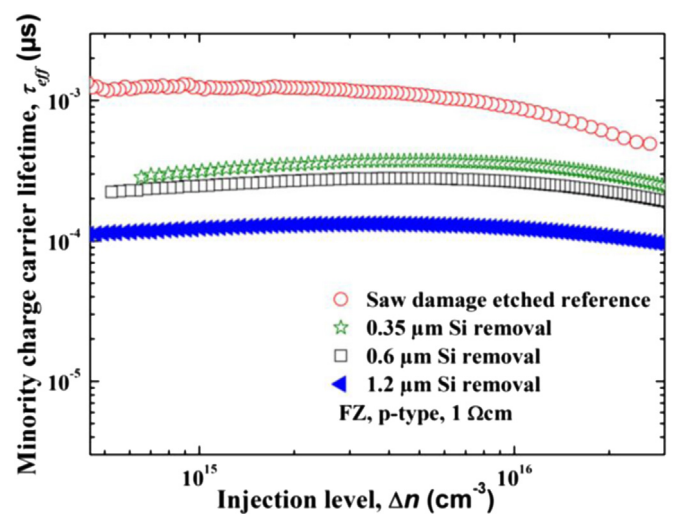


Fig. 2. Plot comparing minority charge carrier lifetimes (τ_{eff}) for symmetrically prepared saw-damage etched reference and nanostructured samples after passivation with AlO_x/SiN_x stack and fast-firing step. The injection level is the excess carrier density (Δn).

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