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Metal-assisted nano-textured solar cells with SiO_2/Si_3N_4 passivation

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ABSTRACT

We demonstrate the fabrication of nano-sized surface textured crystalline silicon by a metal-assisted electroless etching method with nitric acid added as the hole injection agent. This method generates randomly shaped cone-like structures that offer a clear advantage over nanowires by enabling straightforward passivation with standard techniques. Average reflection values as low as 3% have been achieved. Optimizing the thickness of anti-reflective coatings, the doping depth and the screen-printed metal firing process increases the short circuit current of the cell by 0.82 mA/cm^2 over the reference cells, which had a pyramidal texture without nano-texturing.

1. Introduction

In order to enhance the optical absorption in crystalline silicon (c-Si) solar cells, two methods are commonly used in combination: (1) deposition of anti-reflective silicon nitride (SiNx) or oxide (SiOx) films that provide an index matching between the air and the silicon surface, which increases the total number of photons entering the cell; and (2) the formation of light trapping structures, which increase the probability of photon absorption by lengthening the path of the photon travelling inside the wafer. Recently, "black silicon (b-Si)," which exhibits light trapping and anti-reflective behaviour, has been studied by many groups [1,2]. The term b-Si refers to silicon surfaces with a typical surface reflection of less than 5% over a broad spectral range [3]. Several methods have been employed to form b-Si for photovoltaic applications [4–7] and efficiency values ranging from 18.1% to 22.1% have been attained by applying selective emitter and interdigitated back contact technologies, respectively.

Metal-assisted etching (MAE) is a simple, solution based technique for the fabrication of b-Si textured c-Si wafers for solar cell applications [8]. It was reported that b-Si solar cells textured with MAE can have efficiencies comparable to or better than those achieved with standard methods, such as alkaline or acidic texturing schemes [9–11]. In addition, combined applications of conventional and new texturing methods have been introduced for high-performance and low-cost b-Si texturing [12–16].

Beyond its general advantages in optical absorption, nano-sized texturing is also enabling the use of thinner wafers [17,18] as the amount of material lost during nano-texturing, which is critical for thin wafers, is considerably less than that lost during standard texturing, while providing sufficiently good light trapping properties [19]. Nano-texturing also proves to be a successful in forming surface structures on diamond sawn multi-crystalline Si, for which conventional isotropic textures do not work [20].

In earlier studies, we demonstrated the utilization of silicon nanowires (NW) prepared by MAE in the fabrication of mono- and multi-crystalline silicon cells with commercial sizes. However, the solar cells covered with NWs underperformed compared to the standard reference samples due to excessive surface recombination and collection problems [21,22]. It was also revealed that metallization of the structures was challenging on a nanowire decorated surface [23]. In order to enhance the electrical properties without sacrificing the optical performance, we developed a new and modified version of MAE, which enabled the control of the shape of the random nano-structures by tuning the etching solution parameters [24]. Nano-structures with controlled shapes were created when using HNO_3 as an additional oxidative agent. In this way, reflection values lower than for alkaline pyramid textures were obtained with reasonably low surface recombination for wafers with or without an anti-reflection coating. The surface could not be considered as "black" due to the surface smoothing process required for passivation with conventional methods. Furthermore, lower processing costs could be achieved if the silver is recycled, as it is only used as catalyst and not consumed.

In this study, we apply MAE with the addition of HNO_3 to screen-print full Al: BSF mono c-Si solar cells. The process parameters that we

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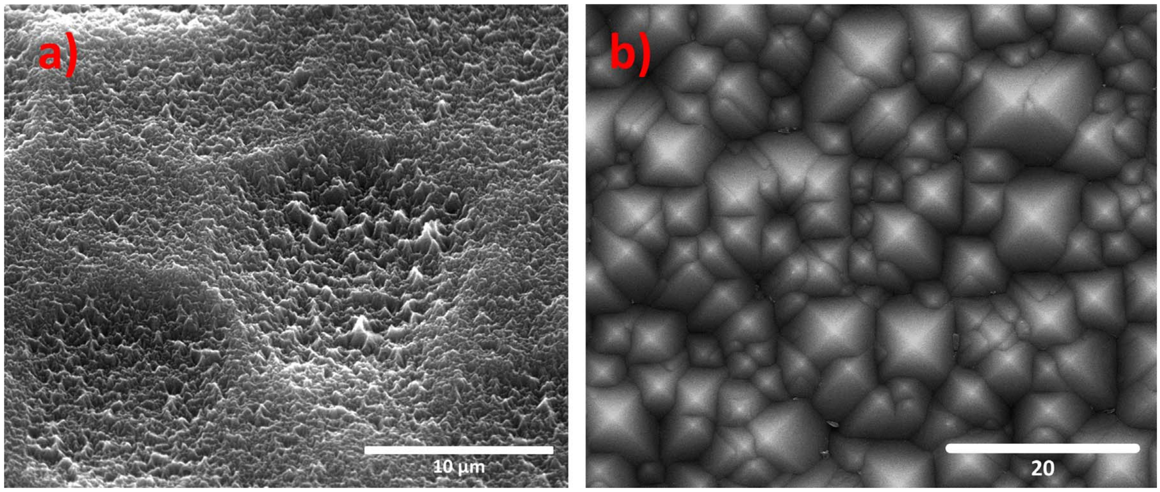

Fig. 1. SEM images of a) nano-textured surface and b) pyramid textured surface.

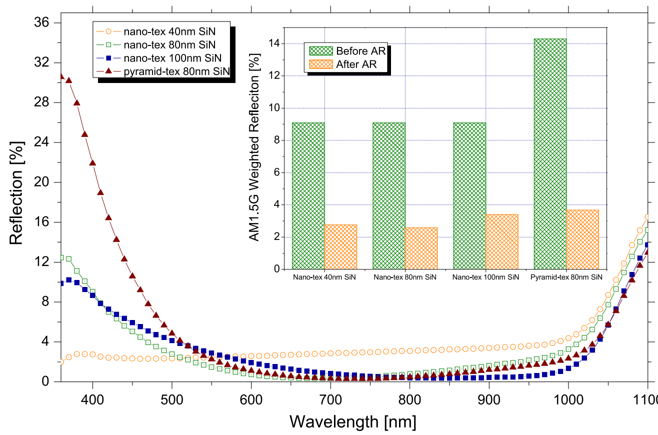

Fig. 2. Reflection spectrum for all samples before and after AR coating together with AM1.5G weighted average reflection added as an inset.

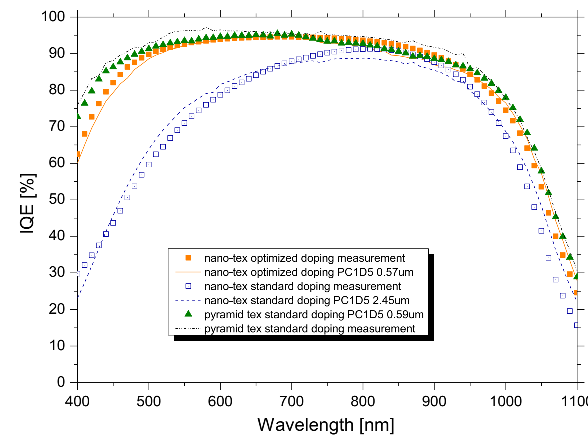

Fig. 3. IQE spectrum for standard doped and optimized doped nano-textured samples together with curves extracted from PC1D5 simulations. Simulations are in good agreement with measured values. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.).

optimized for good optical and electrical properties in our previous study are used here as a surface texturing recipe for the fabrication of mono-c silicon solar cells. An enhancement in cell performance was achieved via metallization and doping optimizations. Ultimately, we obtained 17.80% efficient nano-textured cells, which were 0.1% more efficient than the pyramid-textured reference. Hence, the applicability of nano-texturing in standard mono c-Si solar cell production with conventional passivation layers (SiO_2/SiN_X) was demonstrated.

2. Experimental

2.1. Cell fabrication

For solar cell fabrication, 156 mmx156 mm, 180-µm-thick, solar grade, (100)-oriented mono-crystalline, Czochralski grown silicon wafers with a resistivity of 1–3 Ω cm were used. In order to remove the defects arising from the wire cutting, wafers were first exposed to a saw damage removal step in a solution of 20% KOH at 80 °C for 2 min. Wafers were then divided into two sets: (1) a reference set for pyramid texturing; and (2) a set for black silicon texturing. For the reference set, texturing was carried out in a solution of 3.7% KOH, 3.7% IPA at 70 °C for 45 min. Then, this set was cleaned in a RCA2 solution to pre-condition the wafers' surface before solid-state diffusion.

For the black silicon texturing set, the wafers first went through an RCA2 cleaning step to eliminate the metallic contamination due to alkaline saw-damage etching. Following this step, the oxide grown during RCA process was stripped off with a dilute HF:HCl dip. Metal-assisted electroless etching was then performed with a solution of 0.0011 M $AgNO_3$, 1.36 M HF and 2.89 M HNO_3 as discussed previously [24]. The reactions for Si etching are explained briefly below.

At the cathode, reduction of Ag ions on the surface occurs via the reaction

$$Ag^{+} \rightarrow Ag(s) + h^{+} \tag{1}$$

and reduction of HNO_3, which is faster around the metal nanoparticles, occurs via the reaction

$$HNO_3 + 3H^{+} \rightarrow NO + 2H_2O + 3h^{+} \tag{2}$$

At the anode, dissolution of Si by HF takes place via

$$2Si + 12HF + 6h^{+} \rightarrow 2H_2SiF_6 + 6H^{+} + H_2 \tag{3}$$

while the oxidation of silicon and the dissolution of the formed oxide are obtained by

$$Si + 2H_2O \rightarrow SiO_2 + 4H^{+} + 4e^{-} \tag{4}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{5}$$

Eq. (1) is the mechanism for random silver deposition that provides the injection of holes into Si. Holes injected into Si are used either in the direct dissolution reaction of Si (Eq. (3)) or in oxidation (Eq. (4)) plus etching (Eq. (5)) of Si by HF. When HNO_3 is added to the solution, the rate of hole generation is increased (Eq. (2)) and it becomes higher than the hole consumption around the etch front. This results in