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Pre-texturing multi-crystalline silicon wafer via a two-step alkali etching method to achieve efficient nanostructured solar cells

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ABSTRACT

Alkali solutions are not suitable for texturing multi-crystalline silicon (*mc*-Si) wafer due to the anisotropic etching. In this study, a two-step alkali-etch process is developed to form a flat surface on the wafer, which can be quickly and nearly isotropically etched by immersion in a sodium hydroxide solution, followed by a sodium hydroxide-sodium hypochlorite solution. The etching process leads to the formation of homogenous nanostructure, thereby improving the cell's repeatability and performance by simultaneously increasing its short-circuit current and open-circuit voltage.

1. Introduction

In the past few decades, the photovoltaic (PV) industry witnessed the rapid expansion of silicon-based solar cells, which prompted intension research on the high-quality silicon materials and new techniques to achieve higher power conversion efficiency and lower costs [1–6]. In a *p*–*n* junction based photoelectronic device, the light absorption ability of silicon solar cells enabled by surface textures and antireflection coating is vitally important to achieve high conversion efficiency. However, such absorption ability is still limited due to high reflection at short-wavelength spectra, low absorption coefficient and sensitive to incident angle [7]. Although the multi-layer antireflection coating technique can reduce reflection in whole visible spectra [8], it is not viable for large scale PV production because of its complicate fabrication process and high cost. Black silicon is a promising material for addressing these issues, owing to its excellent light absorption properties. It consists of a silicon surface textured with an optical index-gradient nanostructure by using reactive ionic etching (RIE) or metal-catalyzed chemical etching (MCCE) [9,10].

It has been known that the enhanced light absorption of nanostructured black multi-crystalline silicon (B*mc*-Si) solar cells, results in increased short-circuit current (I_{sc}), which consequently improves the photoelectron conversion efficiency (η) by more than 0.5% [11–13]. However, in *p*-type B*mc*-Si solar cells with oval-like pre-textures (size ~3–5 μm) via acid etching, the nanostructures (size ~150–300 nm) produced at the most electrically sensitive zone (highly doped *n* zone, thinner than 400 nm) will bring some undesired influences to the cell's performance. For instance, the nanostructures also act as carrier recombination centers due to the largely increased surface area of the wafer, which decreases the open-circuit voltage (V_{oc}). It was reported that by combining micron- and nano-textures, a low near-surface recombination could be achieved while maintaining a low surface reflection with a thinner nanostructure layer [14]. In our opinion, such pre-texture is too rough to allow forming a homogenous *p*–*n* junction and contacts. We hypothesize that if a nanostructure can be implanted into another micron-texture with a flatter surface than that of oval-like texture, the recombination rate of photogenerated carriers can be reduced, thereby enhancing the V_{oc} value as well as the I_{sc} value.

Contrary to acid etching, anisotropic alkali etching can produce a texture with pyramidal features on a single crystalline silicon wafer [15]. However, on a multicrystalline silicon, the same etching procedure gives rise to sharp step edges between different crystal grains.

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Table 1
Experimental procedure of *mc*-Si solar cells with different textures.

Sample	H-DRE *mc*-Si	H-DRE B*mc*-Si	N-DRE B*mc*-Si
Step 1	Acid-DRE in HNO_3/HF		Alkali-DRE in NaOH/NaClO
Step 2	/	Nano-texture with MCCE	
Step 3	Fabricating solar cells by using standard process		

Nevertheless, the *mc*-Si wafer can be etched isotropically and polished in NaOH/NaClO mixture solution, thereby obtaining the smooth surface [16]. In this study, a combination process of isotropic alkali etching and MCCE method is used to fabricate *mc*-Si solar cells, and the PV properties of these devices are studied comprehensively. Our results show that, as a result of nanotexturing on a flat surface, the cell's repeatability and performance are improved by simultaneously increasing the I_{sc} and V_{oc} values.

2. Experimental

2.1. Surface texturization

p-type *mc*-Si wafers with a resistivity of 1–3 Ω cm, an area of $156 \times 156\ mm^2$ and a thickness of 180 μm were used in the experiment. Before etching, all raw *mc*-Si wafers produced in same batch were immersed in 4% HF solution for 5 min to remove the native oxide and then rinsed in deionized water. In step 1, two types of *mc*-Si wafers were subject to damage-removal etching (DRE). The wafers etched in the HNO_3/HF mixture solution were labeled as H-DRE, whereas the wafers first etched in NaOH solution and then in NaOH/NaClO solution were labeled as N-DRE.

In step 2, both H-DRE and N-DRE wafers were subject to the same MCCE process, as detailed elsewhere [11,12]. In this process, the wafers were first coated with Ag nanoparticles and then etched in $HF/H_2O_2/H_2O$ mixture solution to form a nano-porous surface. After etching in $NaOH/H_2O$ solution to convert the nanopores into pseudo-pyramids, all the wafers were finally dipped in a 69% HNO_3 solution to remove the remaining Ag nanoparticles. Depended on the procedure used to fabricate them (Table 1), the wafers were labeled as H-DRE *mc*-Si, H-DRE B*mc*-Si and N-DRE B*mc*-Si, respectively.

In step 3, all the wafers were assembled into cells (20 samples each) in a pilot line at Canadian Solar Inc. (CSI) in Suzhou using a standard process, including the formation of a phosphorus diffused n^+ emitter, the removal of edge and back *pn* junctions, the plasma-enhanced-chemical-vapor-deposition of SiN_x antireflection and passivation layer with a thickness ~80 nm, and the screen printing to form front Ag pattern (four bus lines and 91 grid lines) and p^+ back-surface-field Al contact.

2.2. Characterization

The surface and cross-sectional morphologies of the silicon wafers with different textures were characterized using a scanning electron microscope (SEM, Hitachi, S4800, Japan). The optical reflectance spectra were detected using a spectrophotometer equipped with an integrating sphere (Radiation Technology D8, China). The external and internal quantum efficiencies (EQE/IQE) were measured by a quantum efficiency measuring system (QEX7, USA). The electrical performances of solar cells were characterized by a current voltage (I–V) measurement system (Berger PSL-SCD, Germany), WT2000 (Semilab WT2000, Hungary), and Suns-Voc Post-Diffusion Process Control (SINTON WCT-0311, USA).

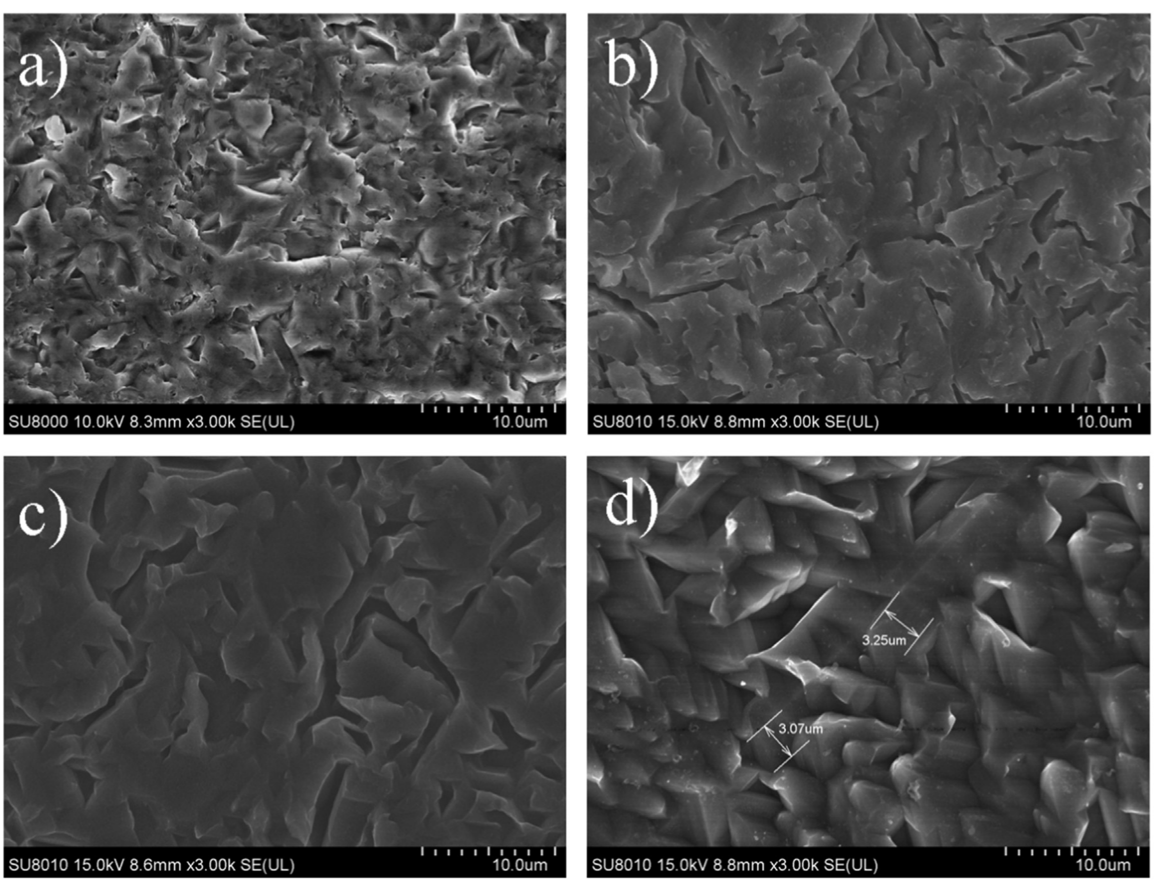

Fig. 1. SEM images of *mc*-Si surfaces textured by immersion in NaOH (5%) solution at 60 °C for (a) 0 s, (b) 60 s, (c) 90 s and (d) 120 s.